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Computer simulations offer immense scope to study the properties of materials. A central goal is the understanding of macroscopic properties on the basis of microscopic material parameters, and the latter are often more accessible to numerical calculation than to experimental measurement. Nevertheless, severe problems confront the computational scientist who is seeking this goal, and the first is provided by the great range of length and time scales involved. For some properties a continuum description of the structure might be appropriate, allowing phenomena to be studied over macroscopic lengths and time scales of the order of seconds or much longer. At the other extreme, we have properties – such as excited states or reactivity – that are determined by the motion of the individual atoms, involving lengths of the order of interatomic separations and time scales of 10^{-13} seconds or shorter. The answers to such questions require a detailed understanding of the geometry and the electronic structure of the material involved.

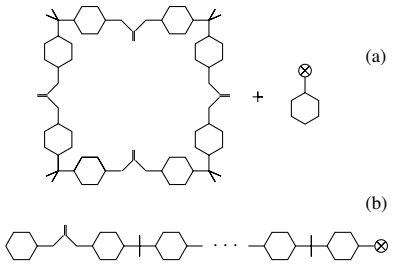
The development of a numerical method that spans these ranges continuously is out of the question and would not make much sense even if possible. Nevertheless, there is much effort devoted at the present time to building bridges between the methods now established in different length and time regimes. These efforts to develop "multi-scale" methods for simulations are reflected in the frequent use of this word in conference announcements.

An idea of the range of scales involved can be obtained from the contributions to this symposium. Molecular dynamics (MD) simulations are now fifty years old and enjoy a conceptual simplicity. The forces in the system are described by (usually) simple force laws or potential functions, and the motions of the components are determined by solving Newton's equations, which introduce a natural time scale. They differ in this regard from Monte Carlo methods, which are purely stochastic and have no builtin time scale. In the contribution of Yamakov *et al.*, MD calculations are performed on polycrystalline aluminium with small grain sizes (under 100 nm). The motion of the grain boundaries is crucial for the mechanical properties of these materials and can be followed with this technique during low-temperature deformation. The calculations provide insight into the motion of the atoms during an extremely complicated process.

The interatomic potential used in these simulations is fitted to experimental data including the elastic constants. The question: "Do the results of the simulations depend on the particular parameterization or the choice of experimental data?" is oft-repeated, but the size and complexity of the simulation make simplifications unavoidable. In the contribution of Brinkmann *et al.*, where metallic glasses and glass-forming melts are simulated under external sheer deformations or reduced dimensions, the force field for $Ni_{0.5}Zr_{0.5}$ and related systems used short-ranged pair potentials based on other calculations. It can be seen that much information can be found from these calculations concerning the effects of changing the temperature, the composition, or the dimensionality of the samples.

It is natural to ask whether molecular dynamics can be used in the context of electronic structure theory. Since the work of Car and Parrinello[1] in 1985 the answer has been "yes". The "Car-Parrinello method" uses the density functional (DF) approach to calculate the energy and forces in the system, using the latter as the basis of molecular dynamics. This approach avoids the parameterization of the force fields mentioned above, but the calculations are numerically very demanding and are limited by present computational technology to around 200 atoms and time scales of the order of 10^{-12} seconds. These restrict greatly the range of phenomena that can be studied, but the predictive capability of the density functional method is widely accepted and has important advantages.

An oral presentation of an application of this method was given by the present author during this symposium[2] and described the reaction of a lithium phenoxide molecule with a ring oligomer of an important industrial polymer, bisphenol A polycarbonate (a). The complex process of breaking the ring and creating a chain with a Li ion at the end (b) is described in detail by these calculations, and the energy barriers found are consistent with experimental evidence. These calculations have been extended to even more complex reactions where little experimental information is available, and the reliable data bases provided by the calculated energy surfaces can be used to develop or refine force field parameters for simulations of much larger systems. Density functional calculations



require an approximation for the exchange-correlation energy, and it would be surprising if the relatively simple functionals often used (the local density approximation and its modifications) could describe all problems of interest. One important problem where the local density approximation gives qualitatively incorrect predictions is the subject of the contribution of Schmid *et al.* The question of whether an effective single-particle theory can describe the antiferromagnetic transition metal oxides has haunted density functional workers for many years, as the DF predictions of metallic behaviour run counter to the insulating state found experimentally. The approach taken by Schmid *et al.* is to separate E_{xc} into *exact* exchange and a DF description of correlation. This work is still in progress, and extensions must be made before a final assessment can be made.

References

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